Supporting Information

Non-invasively visualizing cell-matrix interactions in two-photon excited supramolecular hydrogels

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4. Synthesis and Characterizations                                                           S17

1. General Information

Chemical reagents and solvents were purchased from Aladdin and used without further purification. \(^1\)H NMR and \(^{13}\)C NMR were obtained on a Bruker Advance III 400 Instrument operating at 400 MHz. HRMS were recorded on a Water Q-Tof Mass Instrument. Fluorescence images were taken on a Olympus IX73 microscope and a two photon microscope (A1RMP, Nikon, Tokyo, Japan).

2. Experimental Procedures

SEM: Samples were prepared by depositing dilute solutions (approximately 0.5 mg/ml) of gelators on silicon wafer, freeze dried overnight, and sprayed with a thin gold layer. SEM images were taken on a FEI QUANTA 250 microscope.

Single-photon and two-photon fluorescence microscope: Samples were prepared by placing 200 \(\mu\)L of flocculent hydrogels on a glass slide, washed with deionized water for three times, and then freeze dried.
overnight. Fluorescence images were taken on a Olympus IX73 microscope and a two photon microscope (A1RMP, Nikon, Tokyo, Japan).

**UV-Vis absorption:** The solution ($2 \times 10^{-5}$ mol/L) of G$_1$-G$_3$ were tested using instrument of Lambda 20 from Perkin Elmer, Inc., USA, respectively.

**Fluorescence spectra:** The solution ($2 \times 10^{-5}$ mol/L) of G$_1$-G$_3$ were tested using LS 50B from Perkin Elmer, Inc., USA, respectively.

**Preparation of single crystals G$_2$-G$_3$:** Crystals suitable for X-ray diffraction was obtained by slow evaporation in n-hexane/tetrahydrofuran/dichloromethane (v/v/v 1:1:1) and n-hexane/tetra-hydrofuran (v/v 1:1) solution at room temperature for G$_2$ and G$_3$, respectively.

**Single crystal X-ray diffraction:** Single-crystal data were collected on a Bruker SMART Apex II CCD-based X-ray diffractometer with Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. The empirical absorption correction was applied by SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). The structure was solved using direct method, and refined by full-matrix least-squares on F2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997).

**X-ray powder diffraction (PXRD):** Xerogels and crystals of G$_1$-G$_2$ were tested using a D8 Advance instrument from Bruker-AXS Company.

**Rheology measurements:** The rheological properties of hydrogels G$_1$-G$_3$ were measured with a Rotary Rheometer (Gemini HRnano). The dynamic frequency sweep measurements were performed using a sinusoidal shear strain of constant peak amplitude (0.01%) over a range of frequencies (0.1-100 rads$^{-1}$) at 25°C.
3. Additional Experimental Data and Figures

3.1 Gelation properties of G1–G14.

For 7-substituted coumarin-derived gelators by pyridine (G4–G5, G7–G8, G10–G11, G13–G14), they could not form hydrogels in water/DMSO (99.5%/0.5%) solution at room temperature (RT) by “solvent-mediated” method. While, they can form gels in water/DMSO (50%/50%) under heating (over 50°C) and cooling by “temperature-mediated” method (Figure 1 and S1). The result suggested that gelation property has no direct relationship with 4-methyl coumarin or 4-hydrogen coumarin in those chemical structures. However, if substitute pyridine group was replaced by benzene (G1, G2), the gelation property was closely related with 4-methyl coumarin or 4-hydrogen coumarin. G1 could form hydrogels in water/DMSO (99.5%/0.5%) at room temperature (RT) by “solvent-mediated” method (Figure 1 and S1), while, G2 only self-assembled into hydrogel in water/DMSO (50%/50%) under heating and cooling by “temperature-mediated” method.

For 6-substituted coumarin-derived gelators by pyridine (G6, G9, G12), all of them could self-assemble into hydrogels in water/DMSO (95.5%/0.5%) at room temperature (RT) by “solvent-mediated” method. While, substitute benzene group based gelator (G3) only formed gel in water/DMSO (50%/50%) under heating and cooling by “temperature-mediated” method. Clearly, pyrindine or benzene has influence on the self-assembly ability of gelators. If pyridine or benzene was replaced by other analogous groups (NG1, NG2), they could not form hydrogels either in water/DMSO (99.5%/0.5%) or in water/DMSO (50%/50%) solution, demonstrating the important role of pyridine or benzene groups for this type of gelators. Thus, G1, G6, G9, and G12 should have stronger self-assembly ability in aqueous solution compared with other gelators, which may be ascribed to the different chemical structures of gelators.
**Figure S1** Schematic demonstration of gelators self-assembly in water/DMSO (99.5%w/0.5%w or 50%w/50%w) through C-H-O bonds. G₁, G₆, G₉, and G₁₂ could self-assemble in aqueous solution under room temperature (final DMSO concentration of 0.5%). G₂-G₅, G₇-G₈, G₁₀-G₁₁, G₁₃-G₁₄ only self-assemble into gels in water/DMSO (50%w/50%w) by heating and cooling. NG₁ and NG₂ could not form hydrogels in water/DMSO (99.5%w/0.5%w or 50%w/50%w) solution.
3.2 Photographs of the hydrogels self-assembled from $G_1$ – $G_{14}$.

![Photographs of the hydrogels from $G_1$ – $G_{14}$ before and after UV light irradiation (365 nm).](image)

**Figure S2** Photographs of the hydrogels from $G_1$ – $G_{14}$ before and after UV light irradiation (365 nm).

3.3 Rheological properties of hydrogels $G_1$-$G_3$.

![Rheological measurement of frequency sweep for hydrogels (a):$G_1$; (b):$G_2$; (c):$G_3$ at a strain of 0.01% over a range of 0.1-100 rads$^{-1}$.](image)

**Figure S3** Rheological measurement of frequency sweep for hydrogels (a):$G_1$; (b):$G_2$; (c):$G_3$ at a strain of 0.01% over a range of 0.1-100 rads$^{-1}$. 

6
3.4 The assembly ability of G₁-G₃ in water.

**Figure S4** Optical microscope images of G₁-G₃ assembly in water. The result suggested that G₁ have the strongest capability of self-assembling into fibers but G₂ and G₃ formed crystals. Scale bar = 20 μm.

3.5 Crystal and experimental data of G₂.

**Table S1A** Crystal data and structure refinement for G₂.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₆ H₁₀ O₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>266.24</td>
</tr>
<tr>
<td>Temperature</td>
<td>298(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P 21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a = 6.6490(5) Å  α = 90°</td>
<td></td>
</tr>
<tr>
<td>b = 28.779(2) Å  β = 115.909(3)°</td>
<td></td>
</tr>
<tr>
<td>c = 7.2200(6) Å  γ = 90°</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>1242.70(16) Å²</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.423 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.857 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>552</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.10 x 0.08 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.07 to 68.41°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-7&lt;=h&lt;=8, -34&lt;=k&lt;=34, -8&lt;=l&lt;=8</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>11930 / 2266 [R(int) = 0.0235]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242</td>
<td>99.4 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9346 and 0.8474</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2266 / 0 / 182</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.050</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0355, wR2 = 0.1046</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0423, wR2 = 0.1110</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.0060(9)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.187 and -0.133 e. Å⁻³</td>
</tr>
</tbody>
</table>

**Table S1B** Bond lengths [Å] and angles [deg] for G₂.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-C(7)</td>
<td>1.1978(17)</td>
</tr>
<tr>
<td>O(2)-C(7)</td>
<td>1.3589(16)</td>
</tr>
<tr>
<td>O(2)-C(8)</td>
<td>1.3938(15)</td>
</tr>
<tr>
<td>O(3)-C(10)</td>
<td>1.3788(14)</td>
</tr>
<tr>
<td>O(3)-C(14)</td>
<td>1.3827(16)</td>
</tr>
<tr>
<td>O(4)-C(14)</td>
<td>1.2064(16)</td>
</tr>
</tbody>
</table>
C(1)-C(2)  1.382(2)
C(1)-C(6)  1.386(2)
C(1)-C(7)  1.4816(19)
C(2)-C(3)  1.381(2)
C(2)-H(2A)  0.9300
C(3)-C(4)  1.366(3)
C(3)-H(3A)  0.9300
C(4)-C(5)  1.365(3)
C(4)-H(4A)  0.9300
C(5)-C(6)  1.393(2)
C(5)-H(5A)  0.9300
C(6)-H(6A)  0.9300
C(8)-C(9)  1.3772(18)
C(8)-C(13)  1.3927(18)
C(9)-C(10)  1.3805(18)
C(9)-H(9A)  0.9300
C(10)-C(11)  1.3920(16)
C(11)-C(12)  1.4001(18)
C(11)-C(16)  1.4332(17)
C(12)-C(13)  1.3739(19)
C(12)-H(12A)  0.9300
C(13)-H(13A)  0.9300
C(14)-C(15)  1.4428(19)
C(15)-C(16)  1.3329(19)
C(15)-H(15A)  0.9300
C(16)-H(16A)  0.9300

C(7)-O(2)-C(8)  122.67(11)
C(10)-O(3)-C(14)  121.97(10)
C(2)-C(1)-C(6)  119.46(14)
C(2)-C(1)-C(7)  122.54(13)
C(6)-C(1)-C(7)  118.00(14)
C(3)-C(2)-C(1)  120.13(16)
C(3)-C(2)-H(2A)  119.9
C(1)-C(2)-H(2A)  119.9
C(4)-C(3)-C(2)  120.49(19)
C(4)-C(3)-H(3A)  119.8
C(2)-C(3)-H(3A)  119.8
C(5)-C(4)-C(3)  119.96(16)
C(5)-C(4)-H(4A)  120.0
C(3)-C(4)-H(4A)  120.0
C(4)-C(5)-C(6)  120.61(17)
C(4)-C(5)-H(5A)  119.7
C(6)-C(5)-H(5A)  119.7
C(1)-C(6)-C(5)  119.35(17)
C(1)-C(6)-H(6A)  120.3
C(5)-C(6)-H(6A)  120.3
O(1)-C(7)-O(2)  123.57(13)
O(1)-C(7)-C(1)  125.74(13)
O(2)-C(7)-C(1)  110.69(12)
C(9)-C(8)-C(13)  121.76(12)
C(9)-C(8)-O(2)  124.24(11)
C(13)-C(8)-O(2)  113.90(11)
C(8)-C(9)-C(10)  117.49(11)
C(8)-C(9)-H(9A)  121.3
C(10)-C(9)-H(9A)  121.3
O(3)-C(10)-C(9)  116.32(10)
O(3)-C(10)-C(11)  120.61(11)
Table S1C Geometrical parameters of hydrogen bonds in crystal G₂.

<table>
<thead>
<tr>
<th>D-H−A</th>
<th>D-H(Å)</th>
<th>H−A(Å)</th>
<th>D−A(Å)</th>
<th>D-H−A(deg)</th>
<th>Symmetry-for-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intra C2-H2A...O2</td>
<td>0.93</td>
<td>2.40</td>
<td>2.7136</td>
<td>100</td>
<td>---</td>
</tr>
<tr>
<td>C4-H4A...O4</td>
<td>0.93</td>
<td>2.49</td>
<td>3.2719</td>
<td>142</td>
<td>1-x,1/2+y,3/2-z</td>
</tr>
<tr>
<td>Intra C9-H9A...O1</td>
<td>0.93</td>
<td>2.39</td>
<td>2.8244</td>
<td>108</td>
<td>---</td>
</tr>
<tr>
<td>C12-H12A...O3</td>
<td>0.93</td>
<td>2.53</td>
<td>3.4378</td>
<td>166</td>
<td>-1+x,y,z</td>
</tr>
<tr>
<td>C16-H16A...O4</td>
<td>0.93</td>
<td>2.47</td>
<td>3.3583</td>
<td>160</td>
<td>-1+x,y,z</td>
</tr>
</tbody>
</table>

:: No Classic Hydrogen Bonds Found

Table S1D Short Ring-Interactions with Cg-Cg Distances in crystal G₂.

Analysis of Short Ring-Interactions with Cg-Cg Distances < 6.0 Angstrom

<table>
<thead>
<tr>
<th>Cg(I)</th>
<th>Cg-Cg</th>
<th>Cg(1) [ 1 ] -&gt; Cg(1)</th>
<th>Cg(3)</th>
<th>Cg(3) [ 1 ] -&gt; Cg(3)</th>
<th>Cg(1) [ 1 ] -&gt; Cg(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cg(I)</td>
<td>Cg-Cg</td>
<td>3.8101</td>
<td>3.6290</td>
<td>3.9568</td>
<td>4.8155</td>
</tr>
<tr>
<td>Min or Max</td>
<td></td>
<td>3.629</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.6 Crystal and experimental data of G₃.

**Self-assembly mechanism:** Compound G₃ also gave crystals suitable for X-ray diffraction analysis upon crystallization from n-hexane/tetrahydrofuran solution with the same method to G₂. Colorless single crystals of G₃ belonged to a monoclinic space group P c and no classic hydrogen bonds or solvent molecules were found in self-assembly (Table S2A, S2B, S2C, for crystallographic details). It was found that the main driving forces in the self-assembly process are two types of C-H⋯O intermolecular hydrogen bonds. Firstly, head-tail fashion of one-dimension (1D) supramolecular polymer was formed through the intermolecular hydrogen bonds between the C=O of lactone and a hydrogen of benzene (C5-H5A⋯O4), which have the a bond length of 2.59 Å (H5A⋯O4). Then 1D supramolecular polymeric strands entangled with each other to form 3D crystal networks through intermolecular hydrogen bonds (C10-H10A⋯O1).
between the C=O of benzene and the 8-hydrogen atom of coumarin with the bond length of 2.51 Å (H10A-O1) (Table S2C). In addition, structure analysis of \( G_3 \) shows that there were no \( \pi-\pi \) stacking occurred in the molecular self-assembly (the minimum Cg-Cg distances are > 4.0 Å, Table S2D).

![Crystal culture](image)

**Table S2A** Crystal data and structure refinement for \( G_3 \).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>( C_{17}H_{12}O_4 )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>280.27</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, ( P\ c )</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>( a = 13.1267(4) ) Å, ( \alpha = 90^\circ ) ( b = 3.86890(10) ) Å, ( \beta = 93.9450(10)^\circ ) ( c = 12.7810(4) ) Å, ( \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>647.56(3) Å(^3)</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>2, 1.437 Mg/m(^3)</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.850 mm(^-1)</td>
</tr>
<tr>
<td>( F(000) )</td>
<td>292</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.10 x 0.05 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.37 to 68.13°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-15(&lt;=)h(&lt;=)15, -4(&lt;=)k(&lt;=)4, -15(&lt;=)l(&lt;=)15</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>7022 / 2370 [R(int) = 0.0240]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242</td>
<td>99.3 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.933 and 0.847</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on ( F^2 )</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2272 / 2 / 190</td>
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<td>Goodness-of-fit on ( F^2 )</td>
<td>1.070</td>
</tr>
<tr>
<td>Final R indices [I&gt;2\sigma(I)]</td>
<td>( R1 = 0.0371, ) ( wR2 = 0.1058 )</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>( R1 = 0.0372, ) ( wR2 = 0.1060 )</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.02(18)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.350 and -0.429 e. Å(^-3)</td>
</tr>
</tbody>
</table>

**Table S2B** Bond lengths [Å] and angles [deg] for \( G_3 \).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-C(7)</td>
<td>1.203(3)</td>
</tr>
<tr>
<td>O(2)-C(7)</td>
<td>1.369(3)</td>
</tr>
<tr>
<td>O(2)-C(8)</td>
<td>1.404(2)</td>
</tr>
<tr>
<td>O(3)-C(11)</td>
<td>1.381(2)</td>
</tr>
<tr>
<td>O(3)-C(16)</td>
<td>1.381(2)</td>
</tr>
<tr>
<td>O(4)-C(16)</td>
<td>1.208(2)</td>
</tr>
<tr>
<td>C(1)-C(6)</td>
<td>1.394(3)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.397(3)</td>
</tr>
<tr>
<td>C(1)-C(7)</td>
<td>1.484(3)</td>
</tr>
</tbody>
</table>
C(2)-C(3)  1.389(3)
C(2)-H(2A)  0.9500
C(3)-C(4)  1.382(3)
C(3)-H(3A)  0.9500
C(4)-C(5)  1.395(3)
C(4)-H(4A)  0.9500
C(5)-C(6)  1.389(3)
C(5)-H(5A)  0.9500
C(6)-H(6A)  0.9500
C(8)-C(13)  1.374(3)
C(8)-C(9)  1.391(3)
C(9)-C(10)  1.387(3)
C(9)-H(9A)  0.9500
C(10)-C(11)  1.388(3)
C(10)-H(10A)  0.9500
C(11)-C(12)  1.396(3)
C(12)-C(13)  1.406(3)
C(12)-C(14)  1.455(3)
C(13)-H(13A)  0.9500
C(14)-C(15)  1.347(3)
C(14)-C(17)  1.498(3)
C(15)-C(16)  1.447(3)
C(15)-H(15A)  0.9500
C(17)-H(17A)  0.9800
C(17)-H(17B)  0.9800
C(17)-H(17C)  0.9800
C(7)-O(2)-C(8)  119.02(15)
C(11)-O(3)-C(16)  121.71(15)
C(6)-C(1)-C(2)  119.93(18)
C(6)-C(1)-C(7)  117.98(17)
C(2)-C(1)-C(7)  122.08(17)
C(3)-C(2)-C(1)  119.9(2)
C(3)-C(2)-H(2A)  120.1
C(1)-C(2)-H(2A)  120.1
C(4)-C(3)-C(2)  120.0(2)
C(4)-C(3)-H(3A)  120.0
C(2)-C(3)-H(3A)  120.0
C(3)-C(4)-C(5)  120.56(19)
C(3)-C(4)-H(4A)  119.7
C(5)-C(4)-H(4A)  119.7
C(6)-C(5)-C(4)  119.6(2)
C(6)-C(5)-H(5A)  120.2
C(4)-C(5)-H(5A)  120.2
C(5)-C(6)-C(1)  120.0(2)
C(5)-C(6)-H(6A)  120.0
C(1)-C(6)-H(6A)  120.0
O(1)-C(7)-O(2)  123.21(18)
O(1)-C(7)-C(1)  125.50(19)
O(2)-C(7)-C(1)  111.29(16)
C(13)-C(8)-C(9)  122.07(18)
C(13)-C(8)-O(2)  122.09(18)
C(9)-C(8)-O(2)  115.64(17)
C(10)-C(9)-C(8)  119.40(18)
C(10)-C(9)-H(9A)  120.3
C(8)-C(9)-H(9A)  120.3
C(9)-C(10)-C(11)  118.70(18)
C(9)-C(10)-H(10A)  120.6
Table S2C Geometrical parameters of hydrogen bonds in crystal G₃.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>C5-H5A...O4</td>
<td>0.95</td>
<td>2.59</td>
<td>3.5170</td>
<td>164</td>
<td>-1+x,-1+y,z</td>
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<tr>
<td>C10-H10A...O1</td>
<td>0.95</td>
<td>2.51</td>
<td>3.1452</td>
<td>124</td>
<td>x,2-y,-1/2+z</td>
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</table>

 :: No Classic Hydrogen Bonds Found

Table S2D Short Ring-Interactions with Cg-Cg Distances in crystal G₃.

Analysis of Short Ring-Interactions with Cg-Cg Distances < 6.0 Angstrom

<table>
<thead>
<tr>
<th>Cg(I)</th>
<th>Cg-Cg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cg(I)</td>
<td>Cg-Cg</td>
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<tr>
<td>Cg(I) [1] -&gt; Cg(3)</td>
<td>4.6556</td>
</tr>
<tr>
<td>Cg(3) [1] -&gt; Cg(1)</td>
<td>4.4618</td>
</tr>
</tbody>
</table>

Min or Max 4.462

3.7 Power XRD patterns of crystal and xerogel from hydrogelators G₂ and G₃.

![XRD Patterns](image-url)
**Figure S5** Power XRD patterns of crystals and xerogels self-assembled from hydrogelators a) G$_2$ and b) G$_3$. Here, PXRD patterns of two states could be essentially same with each other, implying the same packing modes in both single crystal and xerogel state.

3.8 Fluorescence spectra of hydrogelators G$_1$-G$_3$.

![Fluorescence spectra](image)

**Figure S6** a) The fluorescent emission spectra of G$_1$-G$_3$ nanofibrous solution, respectively. b) Fluorescence spectra of nanofibrous solution with increasing G$_1$ concentration.

3.9 Fluorescent images of the nanofibers self-assembled from G$_2$, G$_3$.

![Fluorescent images](image)

**Figure S7.** SEM image of G$_2$ and G$_3$ nanofibers. Scale bar = 5 μm. Single-photon fluorescent images of G$_2$ and G$_3$ nanofibers under UV excitation. Scale bar = 300 μm. Two-photon fluorescent images of G$_2$ and G$_3$ nanofibers under NIR excitation. Scale bar = 50 μm.
3.10 Fluorescent images of A549 cells cultured on G₁ hydrogels films.

Figure S8. 2D cell-substrate imaging blue nanofibers under the excitation of a) UV light at the wavelength of 360-370 nm and b) NIR light at the wavelength of 750 nm. Red or yellow A549 cells are excited at the wavelength of 530-550 nm or 544 nm. The images are overlay of the nanofibers and cells at the same sample site. Scale bar = 50 μm.

3.11 Cell viability of A549 cells incubated with hydrogelators G₁-G₃.

Figure S9. After culturing human lung carcinoma (A549) cells in the presence of hydrogelators G₁, G₂, or G₃ (the concentration: 20-200 μM) for 24 hours, over 90% (by CCK-8 assays) of survival cells suggested the good biocompatibility for all of them.
3.12 Two-photon excited fluorescent images of A549 cells cultured in 3D $G_1$ hydrogels.

**Figure S10.** (above) Volume view of 3D cell-substrate imaging. (below) Slices view of the overlaid images of both nanofibers and A549 cells at the same depths. The blue nanofibers are excited by NIR laser at the wavelength of 750 nm. Yellow cells are excited at the wavelength of 544 nm. Scale bar = 20 $\mu$m.
**Figure S11.** The simultaneous confocal fluorescent images of cells and nanofibers in the same scanning transverse section after 8 h culture and the dynamic imaging of cells migrating through 3D nanofibrous structures from 0 to 90 min. Scale bar = 10 μm.

**Table S3.** Coumarin-based supramolecular platform for cell-matrix imaging.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Molecular Structure</th>
<th>Gelation solvent</th>
<th>Temperature (°C)</th>
<th>Cell imaging</th>
<th>Entry</th>
<th>Molecular Structure</th>
<th>Gelation solvent</th>
<th>Temperature (°C)</th>
<th>Cell imaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>G₁</td>
<td><img src="image1" alt="Structure" /></td>
<td>PBS(0.5% MSO)</td>
<td>RT⁺</td>
<td>2D/3D</td>
<td>G₆</td>
<td><img src="image2" alt="Structure" /></td>
<td>PBS(0.5% MSO)</td>
<td>RT⁺</td>
<td>2D/3D</td>
</tr>
<tr>
<td>G₂</td>
<td><img src="image3" alt="Structure" /></td>
<td>PBS(50% MSO)</td>
<td>88°</td>
<td>2D</td>
<td>G₁₀</td>
<td><img src="image4" alt="Structure" /></td>
<td>PBS(50% DM SO)</td>
<td>93 °</td>
<td>2D</td>
</tr>
<tr>
<td>G₃</td>
<td><img src="image5" alt="Structure" /></td>
<td>PBS(50% MSO)</td>
<td>78 °</td>
<td>2D</td>
<td>G₁₃</td>
<td><img src="image6" alt="Structure" /></td>
<td>PBS(50% DM SO)</td>
<td>95 °</td>
<td>2D</td>
</tr>
<tr>
<td>G₄</td>
<td><img src="image7" alt="Structure" /></td>
<td>PBS(50% MSO)</td>
<td>85 °</td>
<td>2D</td>
<td>G₁₅</td>
<td><img src="image8" alt="Structure" /></td>
<td>PBS(0.5% MSO)</td>
<td>RT⁺</td>
<td>2D/3D</td>
</tr>
<tr>
<td>G₅</td>
<td><img src="image9" alt="Structure" /></td>
<td>PBS(50% MSO)</td>
<td>82 °</td>
<td>2D</td>
<td>G₁₇</td>
<td><img src="image10" alt="Structure" /></td>
<td>Methanol</td>
<td>45 °</td>
<td>2D</td>
</tr>
<tr>
<td>G₆</td>
<td><img src="image11" alt="Structure" /></td>
<td>PBS(0.5% MSO)</td>
<td>RT⁺</td>
<td>2D/3D</td>
<td>G₁₈</td>
<td><img src="image12" alt="Structure" /></td>
<td>Methanol</td>
<td>53 °</td>
<td>2D</td>
</tr>
<tr>
<td>G₇</td>
<td><img src="image13" alt="Structure" /></td>
<td>PBS(50% MSO)</td>
<td>87 °</td>
<td>2D</td>
<td>NG₁</td>
<td><img src="image14" alt="Structure" /></td>
<td>Non-gelator</td>
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<tr>
<td>G₈</td>
<td><img src="image15" alt="Structure" /></td>
<td>PBS(50% MSO)</td>
<td>92 °</td>
<td>2D</td>
<td>NG₂</td>
<td><img src="image16" alt="Structure" /></td>
<td>Non-gelator</td>
<td>---</td>
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</tr>
</tbody>
</table>

Gel preparation methods: (a) “solvent-mediated” method; (b) “temperature-mediated” method.
4. Synthesis and Characterizations

**Synthesis of G₁:**

A solution of 7-hydroxy-4-methylcoumarin (1.76 g, 10 mmol) and TEA (1.50 g, 15 mmol) in CH₂Cl₂ (20 ml) was stirred at 0°C for 30 min, then a solution of benzoyl chloride (2.10 g, 15 mmol) in CH₂Cl₂ (5 ml) was added dropwise. The mixture was stirred for overnight at room temperature. The resulting solution was washed three times with water (5 ml), saturated NaHCO₃ solution (5 ml). Then the organic layer was collected and dried over anhydrous Na₂SO₄. Purification with column chromatography (CH₂Cl₂:EA=5:1) gave the product (2.32 g, 83%) as a white powder.

**1H NMR (400 MHz, CDCl₃)** δ = 8.19 (dd, J₁=1.6 Hz, J₂=0.8 Hz, 2H), 7.65 (d, J=8.4 Hz, 2H), 7.53 (t, J₁=8.0 Hz, 2H), 7.22 (m, 2H), 5.28 (s, 1H), 2.45 (s, 3H).

**13C NMR (400 MHz, CDCl₃)** δ = 164.7, 160.7, 154.5, 153.6, 152.2, 134.3, 130.5, 129.1, 129.0, 128.9, 125.7, 118.5, 118.1, 114.8, 110.8. HRMS (ESI) calcd for C₁₇H₁₂O₄ [M+H]+ 280.0736; found 281.0828.

**G₂-G₃** were prepared using the same procedure for G₁.

**Synthesis of G₂:**

7-hydroxycoumarin (1.62 g, 10 mmol), benzoyl chloride (2.10 g, 15 mmol) and TEA (1.50 g, 15 mmol) in CH₂Cl₂ (25 ml) yielded G₂ as white powder (2.12 g, 80%). **1H NMR (400 MHz, CDCl₃)** δ = 8.20 (t, J=3.2 Hz, 2H), 7.65-7.71 (m, 2H), 7.53 (t, J=8.0 Hz, 3H), 7.25 (s, 1H), 7.20 (m, 1H), 6.41 (d, J=9.6 Hz, 1H). **13C NMR (400 MHz, CDCl₃)** δ = 164.7, 160.5, 154.9, 153.7, 143.1, 134.3, 130.5, 129.1, 128.9, 125.7, 118.8, 116.9, 116.3, 110.8. HRMS (ESI) calcd for C₁₆H₁₀O₄ [M+H]+ 266.0579; found 267.0671.

**Synthesis of G₃:**

6-Hydroxy-4-methylcoumarin (1.76 g, 10 mmol), benzoyl chloride (2.10 g, 15 mmol) and TEA (1.50 g, 15 mmol) in CH₂Cl₂ (25 ml) yielded G₃ as white powder (2.46 g, 88%). **1H NMR (400 MHz, CDCl₃)** δ = 8.19 (s, 2H), 7.65 (d, J=7.6 Hz, 1H), 7.53 (t, J=8.0 Hz, 2H), 7.46 (t, J₁=0.8 Hz, 1H), 7.38 (d, J=0.8 Hz, 1H), 7.25 (s, 1H), 6.33 (s, 1H), 2.42 (s, 3H). **13C NMR (400 MHz, CDCl₃)** δ = 165.1, 160.3, 151.6, 150.9, 146.8, 133.9, 130.1, 130.0, 128.8, 128.6, 128.3, 125.3, 120.5, 118.0, 117.3, 115.6, 18.6. HRMS (ESI) calcd for C₁₇H₁₂O₄ [M+H]+ 280.0736; found 281.0812.
Synthesis of $G_4$:

4-Methylumbelliferone (1.76 g, 10 mmol), 2-Picolinic Acid (1.23 g, 10 mmol), EDCI (1.23 g, 10 mmol) and DMAP (60 mg, 0.5 mmol) in CH$_2$Cl$_2$ (20 ml) yielded $G_4$ as white powder (2.44 g, 85.01%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$=8.87(d, $J$=4.0Hz, 1H), 8.30(d, $J$=8.0Hz, 1H), 7.95(t, $J$=2.0Hz, 1H), 7.68(d, $J$=8.0Hz, 1H), 7.60(t, $J$=4.0Hz, 1H), 7.30(d, $J$=2.0Hz, 1H), 6.30(s, 1H), 2.46(d, $J$=1.2Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$= 163.4, 150.4, 146.9, 137.6, 128.0, 126.3, 125.7, 118.4, 114.8, 110.9, 18.9. HRMS (ESI) calcd for $C_{16}H_{12}NO_4$ 282.0766 [M+H]$^+$; found 282.0771.

Synthesis of $G_5$:

To a solution of 7-hydroxycoumarin (1.62 g, 10 mmol), 2-Picolinic Acid (1.23 g, 10 mmol) and DMAP (60 mg, 0.5 mmol) in CH$_2$Cl$_2$ (20 ml) was added EDCI (2.10 g, 11 mmol). The mixture was stirred for 2 hours at room temperature. The resulting solution was washed three times with water (5 ml), saturated NaHCO$_3$ solution (5 ml). Then the organic layer was collected and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under vacuum to give the product $G_5$ as white powder (2.45 g, 91.76%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$=8.87(d, $J$=4.0Hz, 1H), 8.29(d, $J$=7.6Hz, 1H), 7.95(t, $J$=8.0Hz, 1H), 7.72(d, $J$=9.6Hz, 1H), 7.60(t, $J$=4.0Hz, 1H), 7.55(d, $J$=8.4Hz, 1H), 7.3(s, 1H), 7.23(d, $J$=8.0Hz, 1H), 6.43(d, $J$=9.6Hz, 1H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ = 163.4, 160.4, 151.8, 151.3, 150.2, 143.0, 137.6, 128.9, 128.0, 126.3, 118.7, 117.1, 116.4, 110.8. HRMS (ESI) calcd for $C_{15}H_{10}NO_4$ 268.0610 [M+H]$^+$; found 268.0609.

Other gelators were prepared by using the similar above procedure.

Synthesis of $G_6$:

To a solution of 6-hydroxy-4-methylcoumarin (1.76 g, 10 mmol), 2-Picolinic Acid (1.23 g, 10 mmol) and DMAP (60 mg, 0.5 mmol) in CH$_2$Cl$_2$ (20ml) was added EDCI (2.10 g, 11 mmol). The mixture was stirred for 2 hours at room temperature. The resulting solution was washed three times with water (5 ml), saturated NaHCO$_3$ solution (5 ml). Then the organic layer was collected and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under vacuum to give the product $G_6$ as white powder (2.50 g, 88.96%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$=8.84(dd, $J_1$=4.8Hz, $J_2$=0.8Hz, 1H), 8.27(dd, $J_1$=8.0Hz, $J_2$=0.8Hz, 1H), 7.93(dd, $J_1$=7.6Hz, $J_2$=1.2Hz, 1H), 7.58(m, 1H), 7.50(d, $J$=2.4Hz, 1H), 7.43(dd, $J_1$=8.8Hz, $J_2$=2.0Hz, 1H), 7.38(d, $J$=8.8Hz, 1H), 6.32(s, 1H), 2.40(s, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ = 163.9, 160.4, 151.8, 151.3, 150.2,
147.0, 146.9, 137.4, 127.8, 126.1, 125.4, 120.8, 118.2, 117.4, 115.9, 18.7. HRMS (ESI) calcd for C_{16}H_{11}NO_{4} [M+H]^+ 282.0766; found 282.0739.

**Synthesis of G_{7}:**

4-Methylumbellif erone (1.76 g, 10 mmol), Nicotinic acid (1.23 g, 10 mmol), EDCI (1.23 g, 10 mmol) and DMAP (60 mg, 0.5 mmol) in CH_{2}Cl_{2} (20 ml) yielded G_{7} as white powder (2.51 g, 89.32%). ¹H NMR (400 MHz, CDCl₃) δ = 9.4 (s, 1H), 8.89 (dd, J₁ = 4.8 Hz J₂ = 1.6 Hz, 1H), 8.46 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.48-7.51 (m, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.22 (dd, J₁ = 8.8 Hz J₂ = 2.4 Hz, 1H), 6.31 (d, J = 1.2 Hz, 1H), 2.47 (d, J = 1.2 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃) δ = 163.5, 160.5, 154.6, 154.4, 153.0, 152.0, 151.6, 137.9, 125.8, 125.1, 123.7, 118.4, 118.2, 115.0, 110.7, 18.9. HRMS (ESI) calcd for C_{16}H_{12}NO_{4} 282.0755; found 282.0755.

**Synthesis of G_{8}:**

7-hydroxycoumarin (1.62 g, 10 mmol), Nicotinic acid (1.23 g, 10 mmol), EDCI (1.23 g, 10 mmol) and DMAP (60 mg, 0.5 mmol) in CH_{2}Cl_{2} (20 ml) yielded G_{8} as white powder (2.35 g, 88.01%). ¹H NMR (400 MHz, CDCl₃) δ = 9.40 (d, J = 1.6 Hz, 1H), 8.89 (dd, J₁ = 4.8 Hz J₂ = 1.6 Hz, 1H), 8.46 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 9.6 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.20 (dd, J₁ = 8.4 Hz J₂ = 2.4 Hz, 1H), 6.44 (d, J = 9.6 Hz, 1H). ¹³C NMR (400 MHz, CDCl₃) δ = 163.5, 160.4, 154.9, 154.6, 153.1, 151.6, 143.0, 137.9, 129.0, 125.1, 123.8, 118.5, 117.2, 116.5, 110.7. HRMS (ESI) calcd for C_{15}H_{10}NO_{4} 268.0610 [M+H]^+; found 268.0610.

**Synthesis of G_{9}:**

6-Hydroxy-4-methylcoumarin (1.76 g, 10 mmol), Nicotinic acid (1.23 g, 10 mmol), EDCI (1.23 g, 10 mmol) and DMAP (60 mg, 0.5 mmol) in CH_{2}Cl_{2} (20 ml) yielded G_{9} as white powder (2.43 g, 86.47%). ¹H NMR (400 MHz, CDCl₃) δ = 9.40 (d, J = 2.0 Hz, 1H), 8.88 (dd, J₁ = 4.8 Hz J₂ = 1.6 Hz, 1H), 8.45 (dt, J₁ = 8.0 Hz J₂ = 1.6 Hz, 1H), 7.50 (m, 1H), 7.47 (t, J = 1.6 Hz, 1H), 7.40 (d, J = 2.4 Hz, 2H), 6.35 (d, J = 1.2 Hz, 1H), 2.43 (d, J = 1.2 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃) δ = 164.0, 160.3, 154.3, 151.6, 151.4, 151.3, 146.5, 137.8, 125.3, 125.2, 123.7, 120.8, 118.3, 117.3, 116.0, 18.7. HRMS (ESI) calcd for C_{16}H_{11}NO_{4} [M+H]^+ 282.0766; found 282.0757.

**Synthesis of G_{10}:**
4-Methylumbelliferone (1.76 g, 10 mmol), Isonicotinic acid (1.23 g, 10 mmol), EDCI (1.23 g, 10 mmol) and DMAP (60 mg, 0.5 mmol) in CH₂Cl₂ (20 ml) yielded G₁₀ as white powder (2.60 g, 90.59%). ¹H NMR (400 MHz, CDCl₃) δ = 8.89 (d, J = 6.0 Hz, 2H), 8.01 (d, J = 6.0 Hz, 2H), 7.68 (d, J = 8.8 Hz, 1H), 7.26 (d, J = 2.4 Hz, 1H), 7.20 (dd, J₁ = 8.8 Hz J₂ = 2.4 Hz, 1H), 6.31 (d, J = 1.2 Hz, 1H), 2.47 (d, J = 1.2 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃) δ = 163.4, 160.5, 154.4, 152.9, 152.0, 151.2, 136.2, 125.9, 123.4, 118.5, 118.0, 115.0, 110.6, 18.9. HRMS (ESI) calcd for C₁₆H₁₂NO₄ 282.0766 [M+H]+; found 282.0764.

Synthesis of G₁₁:

7-hydroxycoumarin (1.62 g, 10 mmol), Isonicotinic acid (1.23 g, 10 mmol), EDCI (1.23 g, 10 mmol) and DMAP (60 mg, 0.5 mmol) in CH₂Cl₂ (20 ml) yielded G₁₁ as white powder (2.28 g, 85.39%). ¹H NMR (400 MHz, CDCl₃) δ = 8.89 (d, J = 6.0 Hz, 2H), 8.01 (d, J = 6.0 Hz, 2H), 7.73 (d, J = 9.6 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.20 (dd, J₁ = 8.4 Hz J₂ = 2.4 Hz, 1H), 6.44 (d, J = 9.6 Hz, 1H). ¹³C NMR (400 MHz, CDCl₃) δ = 163.4, 160.4, 154.9, 153.0, 151.2, 143.0, 136.2, 129.0, 123.4, 118.4, 117.3, 116.7, 110.7. HRMS (ESI) calcd for C₁₅H₁₀NO₄ 268.0610 [M+H]+; found 268.0607.

Synthesis of G₁₂:

6-Hydroxy-4-methylcoumarin (1.76 g, 10 mmol), Isonicotinic acid (1.23 g, 10 mmol), EDCI (1.23 g, 10 mmol) and DMAP (60 mg, 0.5 mmol) in CH₂Cl₂ (20 ml) yielded G₁₂ as white powder (2.35 g, 83.62%). ¹H NMR (400 MHz, CDCl₃) δ = 8.88 (dd, J₁ = 4.4 Hz J₂ = 1.6 Hz, 2H), 8.01 (dd, J₁ = 4.4 Hz J₂ = 1.6 Hz, 2H), 7.47 (d, J = 2.4 Hz, 1H), 7.40 (m, 2H), 6.36 (d, J = 1.2 Hz, 1H), 2.44 (d, J = 1.2 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃) δ = 163.9, 160.3, 151.6, 151.4, 151.0, 146.4, 136.3, 125.1, 123.2, 120.8, 118.2, 117.2, 116.1, 18.7. HRMS (ESI) calcd for C₁₆H₁₁NO₄ [M+H]+ 282.0766; found 282.0758.

Synthesis of G₁₃:

7-Hydroxy-4-methylcoumarin (1.76 g, 10 mmol), 2-Chloronicotinic acid (1.57 g, 10 mmol), EDCI (1.23 g, 10 mmol) and DMAP (60 mg, 0.5 mmol) in CH₂Cl₂ (20 ml) yielded G₁₃ as white powder (2.67 g, 84.76%). ¹H NMR (400 MHz, CDCl₃) δ = 8.62 (dd, J₁ = 4.8 Hz J₂ = 2.0 Hz, 1H), 8.38 (dd, J₁ = 8.0 Hz J₂ = 2.0 Hz,
1H), 7.68 (d, J = 8.4 Hz, 1H), 7.43 (m, 1H), 7.22 (m, 2H), 6.30 (s, 1H), 2.46 (s, 3H). 13C NMR (400 MHz, CDCl3) δ = 182.0, 158.8, 153.5, 153.2, 152.9, 152.4, 148.9, 141.6, 126.7, 125.3, 123.3, 118.3, 118.1, 114.0, 110.2, 18.2. HRMS (ESI) calcd for C16H10ClNO4 [M+H]+ 316.0386; found 316.0773.

**Synthesis of G14:**

7-hydroxycoumarin (1.62 g, 10 mmol), (1. g, 10 mmol), EDCI (1.23 g, 10mmol) and DMAP (60 mg, 0.5 mmol) in CH2Cl2 (20ml) yielded G14 as white powder (2.13 g, 70.76%). 1H NMR (400 MHz, CDCl3) δ = 8.62 (dd, J1 = 4.8 Hz J2 = 2.0 Hz, 1H), 8.38(dd, J1 = 8.0 Hz J2 = 2.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.43 (m, 1H), 7.22 (m, 2H), 6.43 (d, J = 9.6 Hz, 1H). 13C NMR (400 MHz, CDCl3) δ = 162.5, 160.1, 154.8, 153.8, 152.9, 149.3, 144.2, 141.9, 129.8, 125.6, 123.9, 119.1, 117.4, 116.5, 110.7. HRMS (ESI) calcd for C15H8ClNO4 [M+H]+ 302.0241; found 301.0220.

**Synthesis of NG1:**

7-Hydroxy-4-methylcoumarin (1.76 g, 10 mmol), 2-Pyrazinecarboxylic acid (1.24 g, 10 mmol), EDCI (1.23 g, 10mmol) and DMAP (60 mg, 0.5 mmol) in CH2Cl2 (20ml) yielded NG1 as white powder (2.05 g, 72.69%). 1H NMR (400 MHz, CDCl3) δ = 9.48 (d, J = 1.2 Hz, 1H), 8.88 (d, J = 2.4 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.42 (m, 1H), 6.43 (d, J = 9.6 Hz, 1H). 13C NMR (400 MHz, CDCl3) δ = 162.0, 156.2, 153.7, 152.7, 150.9, 146.8, 145.2, 144.9, 143.6, 125.2, 118.3, 116.4, 114.9, 112.5, 18.9. HRMS (ESI) calcd for C15H10N2O4 [M+H]+ 282.0641; found 282.0635.

**Synthesis of NG2:**

7-hydroxycoumarin (1.62 g, 10 mmol), 2-Pyrazinecarboxylic acid (1.24 g, 10 mmol), EDCI (1.23 g, 10mmol) and DMAP (60 mg, 0.5 mmol) in CH2Cl2 (20ml) yielded NG2 as white powder (1.88 g, 70.15%). 1H NMR (400 MHz, d-DMSO) δ = 9.44 (d, J = 1.2 Hz, 1H), 8.85 (d, J = 2.4 Hz, 1H), 8.81 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.24-7.30 (m, 2H), 6.42 (d, J = 9.6 Hz, 1H). 13C NMR (400 MHz, d-DMSO) δ = 161.8, 159.6, 154.0, 152.6, 148.7, 146.3, 145.0, 143.7, 142.2, 129.7, 118.6, 117.2, 115.9, 110.3. HRMS (ESI) calcd for C14H8N2O4 [M+H]+ 269.0580; found 269.0562.